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Defect configurations of high-*k* cations in germanium

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At germanium/high-*k* interfaces cations and oxygen interstitials can diffuse into the germanium substrate. Here we employ density functional theory calculations to investigate the interaction of a range of such cations (Al, Y, Zr, Nb, La, and Hf) with intrinsic defects and oxygen in germanium. It is predicted that high-*k* cations strongly bind with lattice vacancies, oxygen interstitials, and A-centers. The implications for microelectronic device performance are discussed. © *2012 American Institute of Physics*. [doi:10.1063/1.3679089]

I. INTRODUCTION

Germanium (Ge) was studied in the early days of microelectronics, however, it was abandoned and research focused on silicon (Si) due to its superior native oxide and higher band gap.[1] Today, Ge is being considered as an alternative to Si for applications in future nanoelectronic devices.[1] This because by its higher carrier mobilities and the introduction of high-*k* materials, which allowed the substitution of native oxides.[1] There is a resurgence of interest from the research community into the defect processes in Ge and the Ge/high-*k* oxide interfaces.[1–9]

In Ge the dominant intrinsic defect is the vacancy (*V*), which controls processes such as self-and impurity diffusion and cluster formation.[10–12] Oxygen (O) in Ge can potentially play a significant role in defect cluster formation if one considers its role in related materials such as Si.[13–15] A difference between the two material is that in Czochralski-grown Ge the concentration of O is not as significant as is in Si.[1] Nevertheless, the experimental solubility of O in Ge is of the order 10^{18} cm^{-3} and O can be incorporated into Ge when H_2O vapour (or oxygen gas) is present in the growth atmosphere or maybe *via* diffusion at the Ge/oxide interface.[1,16] O interstitials (O_i) are electrically inactive in Ge and in that sense they are not problematic impurities.[1] The association of vacancies with oxygen in Ge to form A-centers (or VO_i pairs) in Ge has been experimentally[17–21] and theoretically[22,23] studied.

There are presently a number of high-*k* oxide insulators being considered including Al_2O_3,[8] Y_2O_3,[24] ZrO_2,[25] La_2O_3,[26] and HfO_2.[8,27] Research efforts have mainly focused on the Ge volatilization products (and related issues) in the high-*k* oxide[28–30] and on the Ge/high-*k* interface.[31,32] It is anticipated that some cations and oxygen atoms from the high-*k* oxides might diffuse in Ge. Rare earth oxides and Y_2O_3 strongly react with Ge forming stable germanate/Ge interfaces with good electrical quality verified by nearly ideal C-V characteristics in metal oxide semiconductor capacitors (MOSCAPs).[2] Despite the evidence for good interfaces, work reported on transistor performance characteristics is not as promising.[3–5] Especially the *p*-channel mobility of FETs is at the same level as the universal Si/SiO_2 mobility or marginally higher. To explain this transistor behavior, it is anticipated that some rare earth cations and oxygen atoms from the high-*k* oxides might diffuse in Ge in small quantities, although enough to introduce scattering centers which could limit the channel mobility in transistors as already observed. This motivates our studies of possible stable cation complexes with Ge defects or O impurities inside the Ge substrate but close to the interface with the dielectric. Nevertheless, there is no information, to our knowledge, regarding the interaction of high-*k* cations with lattice vacancies and/or oxygen atoms in bulk Ge. The aim of the present study is to bridge this gap by contributing towards a systematic understanding of the role and association of a range of high-*k* cations (Al, Y, Zr, Nb, La, and Hf) with vacancies and oxygen in bulk Ge.

II. METHODOLOGY

The plane wave density functional theory (DFT) code CASTEP was employed for all the calculations.[33,34] The exchange and correlation interactions were described using the corrected density functional of Perdew, Burke, and Ernzerhof (PBE)[35] within the generalized gradient approximation (GGA) and in conjunction with ultrasoft pseudopotentials.[36] The plane wave basis set was expanded to a cut-off of 350 eV, whereas a $2 \times 2 \times 2$ Monkhorst-Pack (MP)[37] k-point grid was used with a 64-atom supercell. The calculations were under constant pressure conditions therefore all the unit cell parameters and atomic fractional coordinates were allowed to relax.

To investigate the energetics of cluster formation we calculated the binding energies of the clusters with respect to their component defects. The binding energy of a substitutional *D* atom to an O_i atom and n *V* to form a $D_mV_nO_i$ cluster in Ge is given by

$$E_b(D_mV_nO_iGe_{N-m-n}) = E(D_mV_nO_iGe_{N-m-n}) - mE(DGe_{N-1}) - E(O_iGe_N) - nE(VGe_{N-1}) + (m+n)E(Ge_N), \quad (1)$$

where $E(D_mV_nO_iGe_{N\text{-}m\text{-}n})$ is the energy of a *N* lattice site supercell (here $N = 64$) containing *N-m-n* Ge atoms, *m D* atoms, one O_i atom and *n V*; $E(DGe_{N\text{-}1})$ is the energy of a supercell containing one *D* atom and *N*-1 Ge atoms;

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$E(O_iGe_N)$ is the energy of a supercell containing one O_i atom and N Ge atoms; $E(VGe_{N-1})$ is the energy of a supercell containing a V and N-1 Ge atoms; and $E(Ge_N)$ is the energy of the N Ge atom supercell. With this definition a negative binding energy corresponds to a defect cluster that is stable with respect to its constituent point defect components.

The simulation methodology and in particular its efficacy, limitations and convergence were discussed in recent work.[11,38] The main issue with DFT calculations based upon the GGA (or the local density approximation) is the underestimation of the formation energies of defects in Ge (or Si or SiGe). This is due to the lack of exact exchange in these functionals.[39] To avoid this hurdle the present paper is addressing binding energies (i.e., differences in energy refer to Eq. (1)) and clusters or pairs in their neutral charge state as they are expected to be less sensitive to systematic errors in the exchange-correlation energy. The supercell size is sufficient as the cations or oxygen atoms are separated from their periodic images by at least six nearest neighbor sites. At these distances, the dopant-dopant interactions of neutral defects in Ge or related materials are in effect zero, and therefore the dopant and its periodic image interactions will not affect the results.[11,40–42]

III. RESULTS

In microelectronic devices, properties can be affected by the distribution of impurities, dopants, and defects. Therefore, processes such as cluster formation can have an impact and must be controlled. In uncapped Ge, there are a number of experimental studies reporting Ge substrate loss during thermal processing.[43–45] In Ge/oxide interfaces (for example, Ge/high-k oxide or Ge/GeO_x/high-k oxide), there have also been numerous reports that during volatilization germanium out-diffuses into the oxide in the form of Ge atoms or as GeO molecules.[30,46–50] This could form lattice vacancies or divacancies (V_2) in Ge among other possible defects. It is also anticipated that cations from the oxides will diffuse into Ge. The interaction of these cations with lattice vacancies, divacancies, and oxygen impurities is discussed below.

A. Cation interactions with *V*

In Ge, vacancies dominate and they readily associate with a number of dopants such as Al, Ga, In, C, Sn, N, P, As, and Sb.[5,11] Table I lists the calculated binding energies for the nearest neighbor (NN) DV pairs [see Fig. 1(a)], the second nearest neighbor (2NN) DV pairs [refer to Fig. 1(b)] and

TABLE I. Predicted binding energies (eV) for the NN DV pairs [see Fig. 1(a)], the 2NN DV pairs [see Fig. 1(b)], and the 3NN DV pairs [see Fig. 1(c)].

Defect pair	NN	2NN	3NN
AlV	−0.40[a]	0.09[a]	0.23[a]
YV	−2.66	−2.71	−0.91
ZrV	−1.89	−2.11	0.22
NbV	1.90	−1.17	0.05
LaV	1.72	−2.17	−0.50
HfV	−1.85	−1.90	0.24

[a]Reference 11.

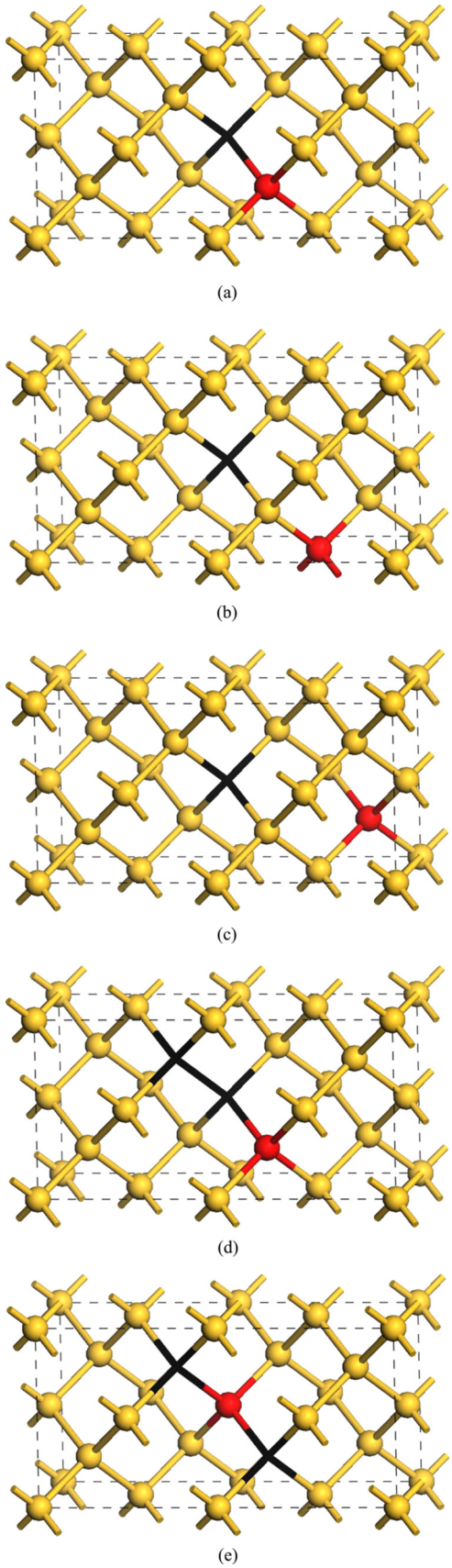

FIG. 1. (Color online) A representation of (a) the NN DV pairs, (b) the 2NN DV pairs, (c) the 3NN DV pairs, (d) the DVV, and (e) VDV cluster configurations. Light grey (yellow) and grey (red) spheres represent the Ge and tetravalent D atoms (i.e., Zr or Hf), respectively, and V are represented by black sticks. For the trivalent D atoms (i.e., Al, Y, Nb, and La), analogous configurations were studied.

TABLE II. Predicted binding energies (eV) for the NN (a) *DVV* [see Fig. 1(d)] and *VDV* [see Fig. 1(e)] clusters.

Defect cluster	NN
V_2	−0.48
Al*VV*	−0.87
Y*VV*	−3.71
Zr*VV*	−2.24
*Nb*V*V*	−1.97
*La*V*V*	−3.37
Hf*VV*	−2.01
*V*A1*V*	−0.29
VYV	−3.69
VZrV	−2.75
VNbV	−2.24
VLaV	−3.44
VHfV	−2.19

the third nearest neighbor (3NN) *DV* pairs [see Fig. 1(c)]. In these configurations, the dopants occupy substitutional positions in the Ge lattice. All the cations considered are bound to the *V* at least at the NN configuration [see Fig. 1(a)]. Part of the binding energy is due to the relaxation of the surrounding lattice around the dopant therefore it is logical that the larger cations (La, Y) are the most bound overall (i.e., if we consider all the possible the NN, 2NN, and 3NN configurations) with *V*. Conversely, Al that is similarly sized to Ge is the least bound. Most *DV* pairs considered ($D = $ Y, Zr, Nb, La, and Hf) have binding energies exceeding −1.8 eV. The magnitude of the binding energies implies that Y, Zr, Nb, La, and Hf will strongly associate with vacancies to form thermally stable clusters. Y and La (i.e., the larger cations) form stable *DV* pairs up to the 3NN [Table II, Fig. 1(c)] and that for Y, Zr, La, and Hf (i.e., the more electropositive cations) the 2NN configurations are energetically favorable [Table II, Fig. 1(b)].

B. Cation interactions with V_2

Recent experimental[51–53] and DFT (Refs. 54 and 55) studies indicate that the divacancy is an important defect pair in Ge. Using the same computational methodology it was previously calculated that the binding energy of V_2 is −0.48 eV.[55] The binding energy of V_2 stems from the reduction of the Ge dangling bonds from eight in the case of two isolated *V* to six when they form a V_2 pair. Table II reports the binding energies of the possible nearest neighbor DV_2 the *DVV* cluster [see Fig. 1(d)] and the *VDV* cluster [see Fig. 1(e)]. The high binding energies of the DV_2 clusters (apart from AlV_2 all other DV_2 can exceed 2 eV) illustrate that V_2 pairs form very stable clusters with cations in Ge. For most of these clusters (i.e., apart AlV_2) the dominant interaction is the attraction between the *D* atom and the *V*. Again the formation of DV_2 clusters can lead to charge scattering centers, which in turn may reduce the mobility.

C. Cation interactions with O_i

It has been previously established that the interfacial reaction at Ge/GeO_2 is an oxidation process.[56] In particular

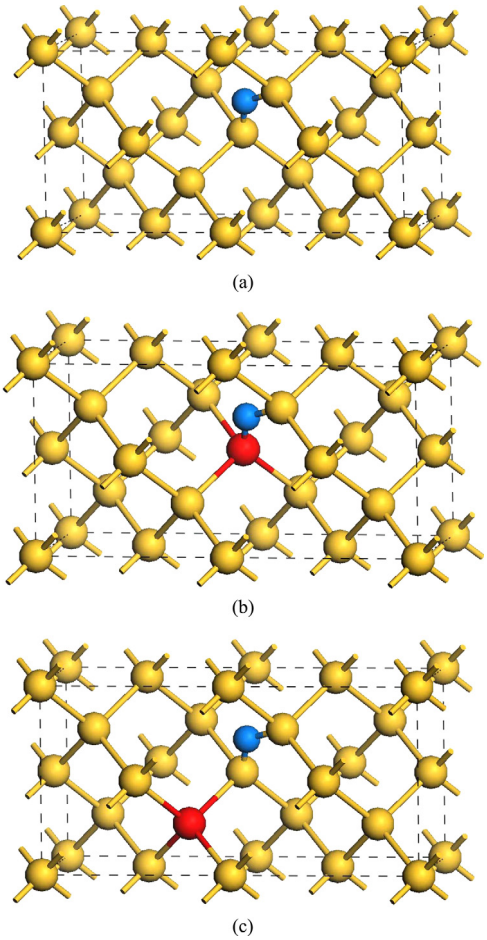

FIG. 2. (Color online) A representation of (a) the O_i, (b) the nearest neighbor DO_i pairs, and (c) the second nearest neighbor DO_i pairs. Light grey (yellow) and grey (red) spheres represent the Ge and tetravalent *D* atoms (i.e., Zr or Hf), respectively, and O_i are represented by dark grey (blue) spheres. For the trivalent *D* atoms (i.e., Al, Y, Nb, and La), analogous configurations were studied.

at the Ge/GeO_2 interface, the reaction takes place through a partial oxidation of the Ge substrate with the O being supplied from the GeO_2. Effectively as Ge is oxidized O_i are incorporated in-between two neighboring Ge atoms [see Fig. 2(a)]. Table III reports the calculated binding energies for the NN DO_i pairs [see Fig. 2(b)] and the 2NN DO_i pairs [see Fig. 2(c)]. Using Eq. (1) (setting $m = 1$ and $n = 0$) the binding energy of these pairs can be calculated. Apart from AlO_i, which is bound only at NN, all the DO_i pairs considered are strongly bound at both NN and 2NN configurations (Table III). Only the HfO_i is more bound at the 2NN [Fig. 2(c)] rather than the NN configuration [Fig. 2(b)]. The magnitude

TABLE III. Predicted binding energies (eV) for the NN DO_i pairs [see Fig. 2(b)] and the 2NN DO_i pairs [see Fig. 2(c)].

Defect pair	NN	2NN
AlO_i	−0.74	0.09
YO_i	−1.88	−1.62
ZrO_i	−1.87	−1.48
NbO_i	−1.90	−1.47
LaO_i	−0.97	−0.83
HfO_i	−0.88	−1.01

of the binding energies implies that if a migrating O_i encounters a cation it will be strongly attracted to it and form a stable DO_i pair. The capture of O_i even at 2NN is strong with the exception of Al for which the 2NN AlO_i pair is not energetically favorable (Table III). The differences for Al must stem from its relatively small size and high electronegativity as compared to the other cations considered here.

D. Cation interactions with A-centers

In previous DFT work using the present methodology the A-center in Ge [see Fig. 3(a)] was calculated to have a binding energy of −0.45 eV (using Eq. (1) with $m=0$ and $n=1$).[23] This is in agreement with the −0.36 eV value by Coutinho *et al.*[22] with the small difference being attributed to the different simulation methodologies. We calculate that if an A-center approaches a cation dopant in Ge the binding energy of the resultant clusters [see Table IV, Figs. 3(b) and 3(c)] is higher than the binding energy of the A-center in undoped Ge. Considering the structure of the diamond lattice there are two possible NN configurations of cation dopant with respect to the A-center. The first configuration involves the cation dopant at a NN site to the vacancy forming a *DV*O cluster [see Fig. 3(b)], whereas in the second configuration the cation dopant is closer to the O_i atom [see Fig. 3(c)].

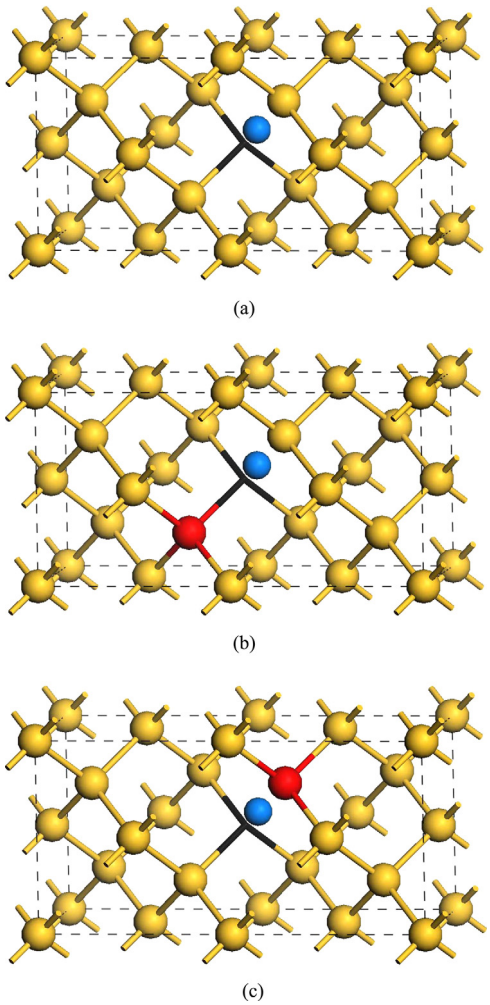

FIG. 3. (Color online) A representation of (a) the A-center in Ge, (b) the nearest neighbor *DV*O cluster, and (c) the *DOV* cluster in Ge. Light grey (yellow) and grey (red) spheres represent the Ge and tetravalent *D* atoms (i.e., Zr or Hf), respectively. O_i are represented by dark grey (blue) spheres and *V* by the black sticks. For the trivalent *D* atoms (i.e., Al, Y, Nb, and La), analogous configurations were studied.

TABLE IV. Predicted binding energies (eV) of the neutral *V*O [see Fig. 3(a)], *V*O pairs in the presence of NN cation to the *V* [*DV*O, see Fig. 3(b)], *V*O pairs in the presence of NN cation to the O_i [*DOV*, see Fig. 3(c)].

Defect cluster	NN
*V*O	−0.45[a]
Al*V*O	−1.65
Y*V*O	−3.97
Zr*V*O	−3.36
Nb*V*O	−3.02
La*V*O	−3.10
Hf*V*O	−2.88
A1O*V*	−1.56
YO*V*	−3.97
ZrO*V*	−3.88
NbO*V*	−3.69
LaO*V*	−2.58
HfO*V*	−3.07

[a]Reference 23.

IV. DISCUSSION

Recent experimental work hints that there is a need of a GeO_2 interface layer in-between the high-*k* oxide and Ge to improve the device properties.[25] It could be that when the high-*k* oxide and Ge are in direct contact the high-*k* cations diffuse into Ge and attract *V*, thus forming charge scattering centers, which in turn may reduce the mobility. The present study is consistent with the formation of *DV* pairs, however, whether these will influence mobility will need to be determined. Additionally, it is clear that the magnitude of the binding energies implies that Y, Zr, Nb, La, and Hf will strongly associate with vacancies to form more thermally stable clusters compared to *DV* pairs previously considered (*D* = B, Ga, In, C, Si, Sn, N, P, As, and Sb), which have binding energies in the range 0.32 eV to −1.05 eV.[5,11] Analogous conclusions can be drawn for the DV_2 pairs.

It should be stressed that there is only limited previous information on the interaction of O_i with impurities in Ge. These studies calculated that the interaction of O_i with dopants such as C, Si, and Sn—which are isovalent to Ge—is repulsive.

The introduction of cations such as Y, Zr, Nb, La, and Hf in Ge can also be useful as a point defect strategy to limit the formation of *V*O pairs. For example, in recent investigations it was demonstrated that the *V*O defect is largely suppressed in Sn-rich doped Si due to the capture of *V* by Sn atoms.[57] This in turn leads to the reduction of the conversion of *V*O to larger clusters due to the formation of Sn*V*O clusters. Based on DFT calculations,[57] it was proposed that doping Si with oversized dopants such as Pb, Zr, or Hf is an efficient way to suppress the *V*O formation. The present calculations provide evidence that Y, Zr, Nb, La, and Hf in Ge result in very stable clusters, which in turn can influence in

an analogous way the formation of *V*O and related defects. This point defect strategy in Ge will need to be experimentally determined.

A limitation of the present calculations is that GGA predicts Ge to be almost metallic. Previous work examined a range of dopant-vacancy clusters in Ge and by comparing to experiment suggested that the trends in binding energy are preserved with the present computational methodology.[10,42] In any case charge states may play a significant role and further work is required to address this issues. The present study provides an initial framework to examine cation, vacancy, and oxygen interactions in Ge.

V. CONCLUSIONS

Density functional theory calculations were used to study the interaction of high-*k* cations with *V*, V_2, O_i, and A-centers in Ge. We predict that these defects and defect pairs are strongly bound with high-*k* cations. The *V*-related clusters may act as charge scattering centers leading to mobility reduction therefore they could have a deleterious impact on the device performance. The binding energies of A-centers in the vicinity of cations in Ge are significantly higher as compared to the binding energies of A-centers in undoped Ge. The association of the high-*k* cations with O_i (and A-centers) and the formation of highly bound clusters can lead to interfacial oxides of composition $D_xGe_yO_z$ in between Ge and the high-*k* oxide. The present contribution is a continuation of efforts to understand the interaction of dopants with oxygen and vacancies in group IV semiconductors and the structure properties relations of semiconductors.[58–60]

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